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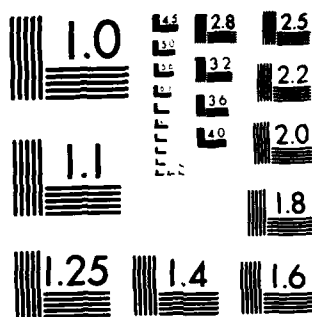
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Interpretation of Auger Lineshapes on Systems With Half-Filled Valence Bands

By

D. E. Ramaker and F. L. Hutson

Department of Chemistry
George Washington University
Washington, D.C. 20052

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**SUMMARY ABSTRACT: Interpretation of Auger Lineshapes
on Systems with Half-filled Valence Bands**

D.E. Ramaker and F.L. Hutson^{*}
Department of Chemistry
George Washington University
Washington, DC 20052

The procedures utilized for quantitative interpretation of CVV Auger lineshapes have become reasonably well established over the years [1]. These involve a self-fold of the occupied one-electron density of states (DOS) appropriate to the final state or ground state (i.e. those appropriate in the absence of a core hole) and inclusion of hole-hole correlation effects by application of the Cini expression,

$$C(N(E)N(E)) = \frac{N(E)N(E)}{(1-\Delta U)N(E)} + \frac{N(E)N(E)}{(1-\Delta U)N(E)} \quad (1)$$

where $I(E)$ is the Hilbert transform and $C(N(E)N(E))$ represents the Cini distortion of the occupied DOS self-fold, $N(E)N(E)$. The quantity ΔU equals $U_{ii}-U_{ii}$, where U_{ii} and U_{ii} are the effective Coulomb repulsions of two holes in the same orbital, and in nearest neighbor orbitals, respectively. ΔU is usually determined empirically from the best fit to the experimental lineshapes. These procedures are illustrated schematically in Fig. 1a for a single band rectangular DOS. In a multi-band system, e.g. having an s and p valence band, the total lineshape consists of the sum of the s, s, s, and p, p components multiplied by the appropriate atomic Auger matrix element, where eq.(1) is applied to each of the individual components.

The procedure described above is consistent with the final state (FS) rule [2], which indicates that the shapes of the individual components are determined by the DOS appropriate to the final state; however, their relative intensities are determined by the DOS appropriate to the initial core hole state. The FS rule is derived using the hole picture, i.e. it enumerates the final- and initial-state holes, and includes

hole-hole coupling in the final state, hence the name FS rule. By enumerating the electrons instead, we can similarly derive an initial state (IS) rule, which prescribes the same as the FS rule, except now it indicates electron-electron coupling in the initial state.

The well-known two-electron Auger matrix element implies the validity of a two-particle coupling scheme. Clearly a two-electron coupling scheme is more appropriate when the band is nearly empty, and a two-hole coupling scheme more appropriate when the band is nearly filled. We conclude that the IS rule is more applicable for less than or equal to half filled bands, and the FS rule for greater than half-filled bands. Furthermore, one can think of the sign of ΔU being positive for two holes and negative for two electrons, since highly correlated holes in the final state lower the Auger kinetic energy, and highly correlated electrons in the initial state raise the Auger kinetic energy. Thus, the correlation of two holes in an otherwise filled band can be treated the same as two electrons in an otherwise empty band, namely by eq. (1), but with the sign of ΔU changed. This is illustrated schematically in Fig. 1 for a single-band rectangular DOS. Consistent with the IS rule, Eq. (1) is applied to the total DOS self-fold, and then only that part which projects onto the initially occupied self-fold remains as the Auger lineshape. This has the effect of both reducing the Auger intensity, and distorting the lineshape, but in the opposite direction to that for the nearly filled band case, when the FS rule is applicable.

This FS-IS theory is utilized to interpret the Auger lineshapes of three widely different systems; namely the C KVV Auger lineshapes of benzene and diamond, and the $L_{2,3}VV$ lineshapes of the first row transition metal series. The separation between the σ and σ^* orbitals in benzene is large so that the σ orbitals can individually be regarded as filled orbitals in the initial Auger state, hence the FS rule is appropriate. On the other hand, the separation between the π and π^* orbitals is much smaller, so that all of the π and π^* orbitals together must be

treated as a single band. In this case the π band is half filled in the initial state and the IS rule is more appropriate. The $\sigma\sigma$ and $\pi\pi$ contributions to the benzene lineshape do indeed show distortions consistent with positive and negative ΔU values, respectively [3]. The polyacetylene like chains on the (111) - (2 x 1) reconstructed surface of diamond, consistent with Pandey's π -bonded chain model, provide a $\pi\pi$ contribution near the top of the diamond lineshape. In this case the $\sigma\sigma$ bulk contribution shows distortions consistent with the FS rule, and the $\pi\pi$ surface contribution is significantly reduced in intensity consistent with the IS rule [3]. Finally, the $L_{2,3}VV$ Auger lineshapes of the transition metals on the left side show negative ΔU distortions, and those on the right show positive ΔU distortions [4]. This is consistent with the IS rule for the less than half-filled d band on the left, and with the FS rule for the greater than half filled d band on the right.

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- *Supported in part by the Office of Naval Research
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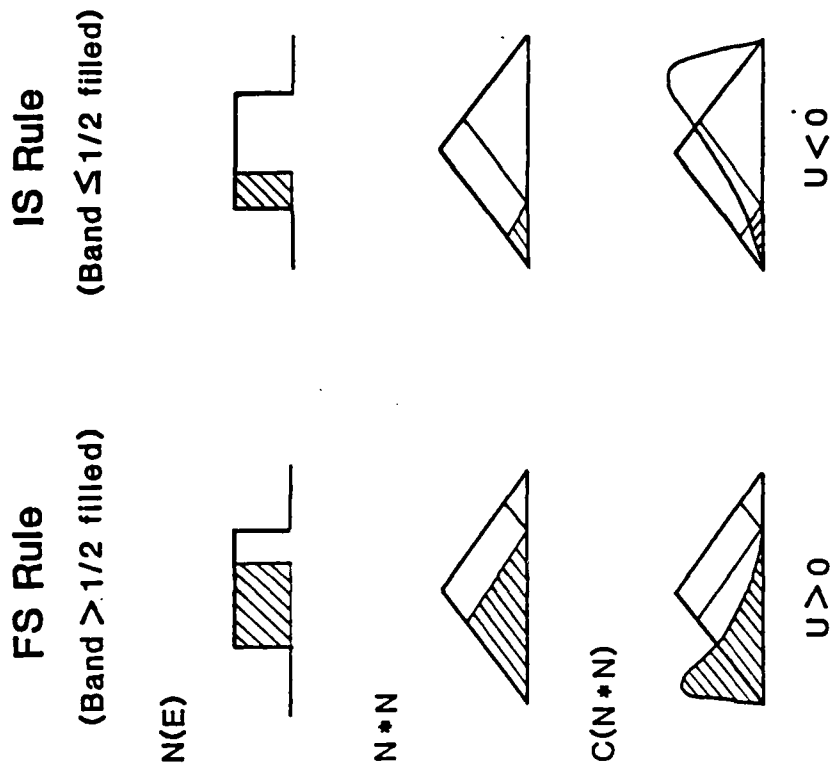


Figure Caption

Fig. 1 Schematic illustration of the final (FS) and initial (IS) state rules applied to a single band rectangular DOS, $N(E)$, with greater and less than half-filled valence bands, respectively. The DOS self-fold, $N(N)$, and the Cini self fold, $C(N(N))$, are also indicated. The cross-hatched areas show the occupied portions of N and $N(N)$, and the resultant Auger lineshape in $C(N(N))$.

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